

Theoretical investigations of the molecular conformation and reorganization energies in the organic diamines as hole-transporting materials

Jiunn-Hung Pan,^{1*} Yu-Ma Chou,² Houn-Lin Chiu³ and Bo-Cheng Wang^{1*}

¹Department of Chemistry, Tamkang University, Tamsui 251, Taiwan

²Department of Physics, Chinese Culture University, Taipei 110, Taiwan

³Department of Chemistry, National Kaohsiung Normal University, Kaohsiung 802, Taiwan

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ABSTRACT: Recently, organic diamine compounds have been widely used as hole-transporting materials. In this work, DFT B3LYP method with the 6-31G^{*} basis set was performed to investigate the influence of molecular conformation on the reorganization energy of a series of tetra(aryl)benzidine-based hole-transport materials. The results indicate that there are two types (i.e., ISB and BD/TPD) of geometric differences of the organic diamines with the relaxation processes. The reorganization energy of the ISB type is lower than that of the BD/TPD type. For the ISB type, the terminal phenyl moiety of the molecular framework plays an important role in determining the Marcus-type reorganization energy and the central biphenyl moiety does not. A methyl group attached to a terminal phenyl can be used to tune the reorganization energy. According to the statistical analysis, four geometric parameters could affect the reorganization energy of the BD/TPD type. The conformation of either the central biphenyl or the terminal phenyl moiety of the BD/TPD type determines the Marcus-type reorganization energy associated with the charge transport process at the molecular level. Presumably, this calculation can be employed to predict the electroluminescence (EL) character of the other organic diamines and to improve the design of new hole-transporting materials in organic light-emitting devices (OLEDs). Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: DFT; TPD

INTRODUCTION

Organic diamines, e.g., *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-([1,1'-biphenyl])-4,4'-diamine (TPD), were used as hole-transporting materials in a wide variety of applications from the Xerox process to multi-layer organic light emitting diode-based devices.^{1–4} Since their discovery,¹ thin multi-layer organic light-emitting devices (OLEDs) were recognized as a potential technology for the next generation flat-panel display devices.⁵ The simplest multi-layer OLED consists of an indium tin oxide (ITO) anode, an electron-transporting layer (ETL), and hole-transporting layer (HTL) where TPD is a prototype of a good HTL material, and a Mg–Ag cathode, in which HTL or/and ETL can act as the emitter. Criteria for good HTL materials are lower energy barrier to the hole injection from the anode, higher mobility, and thermal stability in the amorphous state.^{6–12} In particular, there are many potential applications in the

synthesis of organic hole-transporting devices. An important research frontier is to investigate the fundamental mechanism of charge transport in these materials;^{11–15} however, little is known even for simple molecules. Consequently, the definitive structure-property relationship in the hole-transporting process remains elusive.

During the last decade, there have been few reports on the structure-property issues emphasizing geometric and electronic changes with hole transport phenomena for triphenylamine (TPA) derivatives.^{16–25} Reorganization energies of some amines with a general formula of $\text{NMe}_n\text{Ph}_{3-n}$ as hole-transporting materials were calculated to show that the total energy increased with increasing n .¹⁶ Sakanoue *et al.*¹⁷ proposed similar results concerning the relationship between molecular geometry and the hole-transport property for TPD and its analogs. A decreasing trend was found for reorganization energies (λ) as going from TPD, *N,N'*-dimethyl-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine, *N,N,N',N'*-tetraphenyl-1,1'-biphenyl-4,4'-diamine. This shows that the structural change near the amine N atom upon ionization is one of the important factors in determining the hole mobility.¹⁷ Malagoli and Brédas¹⁸ showed that TPA and TPD have

*Correspondence to: J.-H. Pan or B.-C. Wang, Department of Chemistry, Tamkang University, Tamsui 251, Taiwan.
E-mails: petersonpan@yahoo.com.tw; bcw@mail.tku.edu.tw

different hole-transporting properties and the biphenyl segment plays a significant role in the latter compound. The hole mobilities for a series of TPD derivatives with amino groups were studied systematically based on the Marcus theory,²⁰ and these results showed that the reorganization energy (λ_+) was dependent on the attached biphenyl moiety which contributed predominantly to its HOMO, and the compounds containing biphenyl groups with or without amino groups, had larger reorganization energies than those of the other compounds. Low *et al.*²⁵ proposed that the conformation of the biphenyl moiety of the molecular framework plays a significant role in determining the Marcus-type reorganization energy associated with the hole-transporting processes at the molecular level. Therefore, in the case of TPD as hole-transporting material, the key geometrical parameters (Fig. 1) can be considered in three key torsion: the bond length and the torsional angle between the ring system of the biphenyl

moiety, i.e., the relative orientation of rings A and B [Fig. 1(a)]; the relative orientation of the NPh₂ system with respect to the biphenyl moiety, i.e., the bond length between central amine N atom and ring A and the torsional angle between NPh₂ system and ring A [Fig. 1(b)]; the relative orientation of the terminal phenyl rings (ring C) with respect to the planar conformation about the amine N atom, i.e., the bond lengths N—C_a and N—C_b and the torsional angle between ring C and the N atom [Fig. 1(c)]. In order to gain a more comprehensive understanding of the reorganization energy associated with the charge transfer process and how it is influenced by conformational changes in the molecular structure, in this work, we selected a series of compounds, as shown in Fig. 2, based upon the TPD framework in which methyl groups are used to control the relative orientation of various phenyl ring systems, and the three key torsional modes. Furthermore, we also report the reorganization energies for TPA and biphenyl-4,4'-diamine (BD) including the widely used hole-transport materials such as TPD, N4,N4'-Di-naphthalen-1-yl-N4,N4'diphenyl-biphenyl-4,4'-diamine (NPB), and 1,4-bis-(carbazolyl) biphenyl (CBP) and 1,4-bis(iminostilbenyl) biphenyl (ISB).

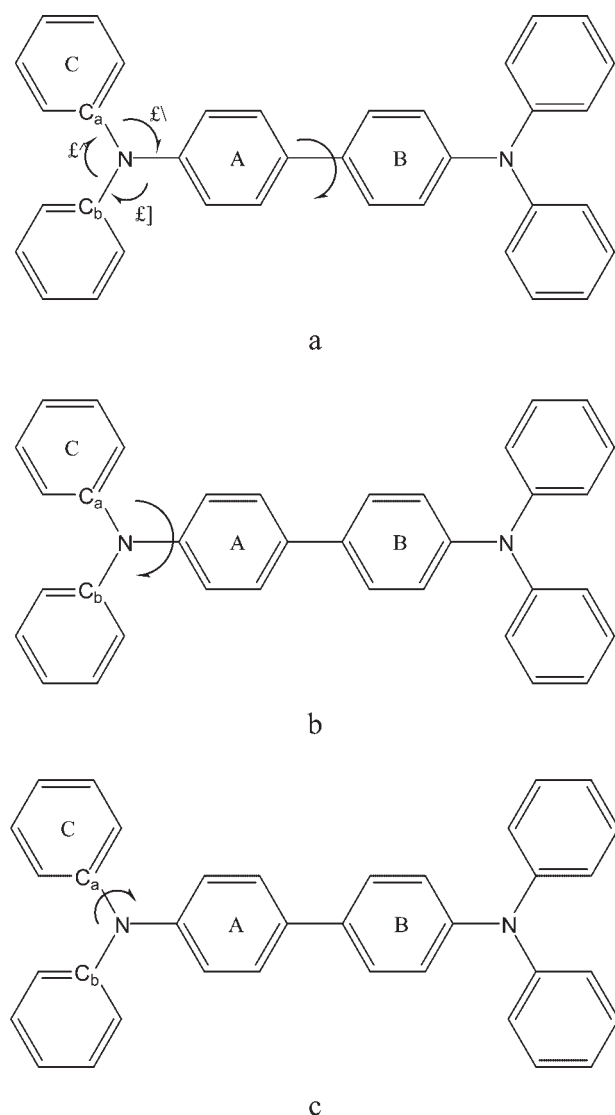


Figure 1. Key torsional modes for tetra(aryl)benzidine (compound **1**).

METHODOLOGY

The thermal and electronic properties of TPD and its analogs have been experimentally determined.^{23–27} In the present work, the energies corresponding to the neutral and the cationic states were generated based on the optimized structure for each state. The reorganization energy consists two terms corresponding to the geometry relaxation energies upon going from the neutral to the cationic states and vice versa:

$$\lambda_+ = \lambda_1 + \lambda_2 \quad (1)$$

$$\lambda_1 = E^+(M) - E^+(M^+) \quad (2)$$

$$\lambda_2 = E(M^+) - E(M) \quad (3)$$

where $E(M)$ and $E^+(M^+)$ are the ground state energies of the neutral and cationic states, respectively. $E^+(M^+)$ is the energy of neutral molecule at the optimal cationic geometry. $E^+(M)$ is the energy of the cationic state at the optimal geometry of the neutral molecule, as shown in Fig. 3. Besides the reorganization energy for hole transporting (λ_+), the ionization potential (I_p) was also calculated as following:

$$I_p = E^+(M) - E(M) \quad (4)$$

The calculated reorganization energy for hole transport (λ_+) is sensitive to the calculation method. For instance, the calculated λ_+ 's of aniline compounds are 0.529 and 0.929 eV at the DFT B3LYP/3-21G and HF/6-31G* levels, respectively.¹⁷ Brédas and co-workers^{28,29} presented a good calculated result, calculated by DFT

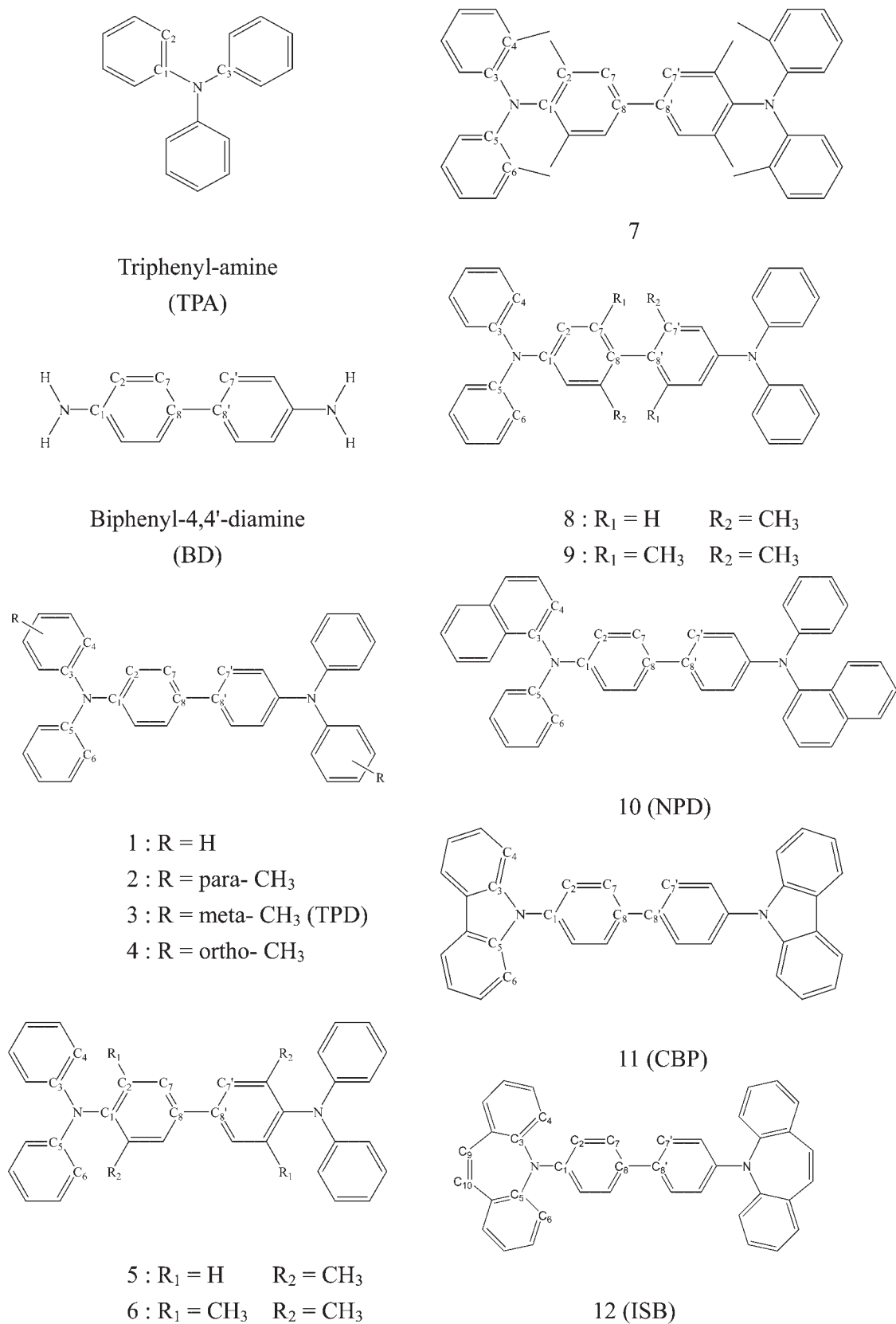


Figure 2. Molecular structures of TPA, BP, tetra(ary)benzidine, compound **1** and its analogs.

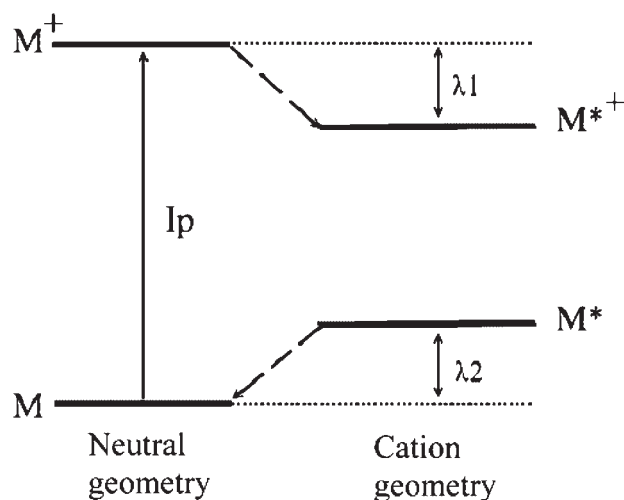


Figure 3. Energies for a compound involved in the vertical transition.

B3LYP method, to reproduce experimental data (gas-phase ultraviolet photoelectron spectra) in oligoacenes. In order to select an appropriate calculation method in this study, we carried out preliminary calculation of the reorganization energy for hole transport (λ_+) of compound **1** using the DFT B3LYP methods with 3-21G, 3-21G*, 6-31G, 6-31G*, and 6-31G**. The calculated results for compound **1** are shown in Table 1. As expected, the calculated reorganization energies for hole transport (λ_+) in compound depend on the selected calculation method. Comparing the calculated reorganization energies (λ_+), DFT B3LYP methods with the 6-31G* and 6-31G** basis sets produce similar results. Because of CPU time limitations, we selected the DFT B3LYP methods with the 6-31G* for the reorganization energy calculations. In this work, all the calculations were made using the DFT B3LYP method with the 6-31G* basis set and was performed using GASSIAN 03 package.³⁰

In order to investigate the major influences of the geometric parameters on the reorganization energy of TPD and its analogs, the Multiple Linear Regression method (MLR), which is based on the numerical technique of least-squares fitting, analyzes the relationship between the dependent variable (reorganization energy)

and the independent variables (p , i.e., the difference in geometric parameters between the neutral and the radical-cation states), is one of our chosen methods.³¹ Indeed, the correlation coefficient (R^2) could be abnormally large if there are a few data points but numerous independent variables. Therefore, the adjusted coefficient ($(R_{\text{adj}})^2$) can be used as:

$$(R_{\text{adj}})^2 = 1 - [(n - 1)/(n - p - 1)](1 - R^2) \quad (5)$$

where n and p are the data point and the independent variable, respectively. In this work, MLR was performed in the Cerius² package.³²

RESULTS AND DISCUSSION

Optimized geometry

The optimized geometrical parameters for TPD and its analogs in neutral and cationic states are collected in Table 2a–2e. For all molecules, the optimized geometries for the neutral and cationic states are all planar around the central amine N atom as judged from the sum of calculated bond angles ($\alpha + \beta + \gamma$), being 360° (Fig. 1).

In order to understand the conformation change during the hole-transport process between the molecules and their segment, the results of the geometry optimizations for TPA, BD, and compound **1** are presented in Table 2a, in which their geometries both for the neutral and cationic states are also studied. For the geometrical parameters of neutral state TPA, three calculated N—C bond lengths and the related torsional angles are 1.422 Å and 41.87°, respectively. The geometrical structure of the radical-cation differs slightly from the neutral one; the torsional angles of phenyl groups decrease to 38.96°, and the N—C bond length decreases to 1.414 Å. Thus, the geometry of TPA in radical-cation state is more planar than that in the neutral state. These calculation results are in excellent agreement with the experimental X-ray crystal structure,³³ *ab initio* HF³⁴ and DFT^{16,18,20} calculations. For compound BD, the inter-ring distances C₈—C₈' are 1.482 and 1.440 Å in the neutral and cationic states, respectively, and the torsion angle C₇—C₈—C₈'—C₇' are 36.08 and 17.69° in each state. The C—N distances are 1.370 and 1.340 Å in the neutral and cationic states, respectively; and the torsion angles H—N—C₁—C₂ are 0.56 and 0.06° (Table 2a) in the neutral and cationic states. Thus, there is a more planar structure for compound BD in a radical-cation state than that in a neutral state. These calculation results are also in excellent agreement with the previous DFT calculations.²⁰ For compound **1**, in the terminal phenyl ring and N atom, the bond lengths N—C₃ and N—C₅ of the structural geometries increase from 1.420 Å in the neutral state to 1.430 Å in the cation state, but the bond length N—C₁ decreases. The C₁—N—C₃—C₄ and C₁—N—C₅—C₆ torsional angles of the structural geometries in the radical-cation state increase

Table 1. Calculated reorganization energies for hole transport (ev) of compound **1**

	DFT B3LYP method				
	3-21G	3-21G*	6-31G	6-31G*	6-31G**
λ_+	0.2659	0.2659	0.2651	0.2723	0.2794
λ_1	0.1371	0.1371	0.1384	0.1410	0.1452
λ_2	0.1288	0.1288	0.1267	0.1313	0.1342

Table 2a. Calculated geometrical parameters of TPA, BD, and compound **1** both for the neutral and cationic states^a

Structural ^a parameter	TPA		BD ^b		1	
	Neutral	Cationic	Neutral	Cationic	Neutral ^c	Cationic ^c
N–C ₁	1.422	1.414	1.370	1.340	1.418	1.387
N–C ₃	1.422	1.414			1.420	1.430
N–C ₅	1.422	1.414			1.420	1.430
C ₇ –C ₈			1.406	1.431	1.406	1.419
C ₈ –C _{8'}			1.482	1.400	1.480	1.455
C ₁ –N–C ₃ (α)	120.00	120.00			120.24	121.06
C ₁ –N–C ₅ (β)					120.24	121.06
C ₃ –N–C ₅ (γ)					119.50	117.87
C ₁ –N–C ₃ –C ₄					43.05	49.00
C ₁ –N–C ₅ –C ₆					43.05	49.00
C ₃ –N–C ₁ –C ₂	41.87	38.96			37.72	35.79
C ₇ –C ₈ –C _{8'} –C _{7'}			36.08	17.69	36.57	22.16

^a For the bond designation as shown in Fig. 1. The bond lengths are in Å and bond angles in (degree).

^b Calculated geometric parameters for compound BD which are not shown in this table: H–N–H = 117.79°, H–N–C₁ = 121.12°, and H–N–C₁–C₂ = 0.56° in the neutral state; and H–N–H = 117.00°, H–N–C₁ = 120.76°, and H–N–C₁–C₂ = 0.06° in the cationic state.

Table 2b. Calculated geometrical parameters of compounds **2–4** for the neutral and cation states^a

Structural parameter	2		3		4	
	Neutral	Cationic	Neutral	Cationic	Neutral	Cationic
N–C ₁	1.419	1.388	1.419	1.387	1.417	1.383
N–C ₃	1.423	1.430	1.423	1.432	1.433	1.442
N–C ₅	1.421	1.431	1.422	1.431	1.421	1.430
C ₇ –C ₈	1.406	1.419	1.406	1.419	1.407	1.420
C ₈ –C _{8'}	1.480	1.455	1.480	1.455	1.482	1.455
C ₁ –N–C ₃	120.01	121.01	120.10	121.06	119.35	122.06
C ₁ –N–C ₅	120.12	121.03	120.09	121.09	121.20	120.59
C ₃ –N–C ₅	119.84	117.95	119.81	117.85	118.54	117.30
C ₁ –N–C ₃ –C ₄	43.78	47.86	42.03	49.11	64.62	65.22
C ₁ –N–C ₅ –C ₆	40.45	48.93	42.13	48.89	32.44	44.02
C ₃ –N–C ₁ –C ₂	39.43	26.55	40.56	25.85	28.54	21.01
C ₇ –C ₈ –C _{8'} –C _{7'}	34.00	22.51	36.01	22.32	35.85	19.20

^a For the bond designation as shown in Fig. 1. The bond lengths are in Å and bond angles in (degree).

Table 2c. Calculated geometrical parameters of compounds **5–7** for the neutral and cationic states^a

Structural parameter	5		6		7	
	Neutral	Cationic	Neutral	Cationic	Neutral	Cationic
N–C ₁	1.430	1.405	1.436	1.422	1.431	1.409
N–C ₃	1.419	1.423	1.418	1.418	1.431	1.431
N–C ₅	1.422	1.423	1.418	1.418	1.431	1.431
C ₇ –C ₈	1.404	1.413	1.402	1.408	1.400	1.409
C ₈ –C _{8'}	1.483	1.462	1.484	1.470	1.483	1.465
C ₁ –N–C ₃	119.52	120.88	118.87	119.55	121.13	121.39
C ₁ –N–C ₅	118.50	119.34	118.86	119.56	121.13	121.39
C ₃ –N–C ₅	121.01	119.31	122.27	120.89	117.73	117.23
C ₁ –N–C ₃ –C ₄	29.12	37.29	32.19	35.75	46.50	47.66
C ₁ –N–C ₅ –C ₆	43.60	46.50	32.19	35.86	46.50	47.66
C ₃ –N–C ₁ –C ₂	63.46	48.61	68.76	57.85	51.57	46.35
C ₇ –C ₈ –C _{8'} –C _{7'}	36.14	23.80	36.76	28.20	37.58	25.94

^a For the bond designation as shown in Fig. 1. The bond lengths are in Å and bond angles in (degree).

Table 2d. Calculated geometrical parameters of compounds **8** and **9** for the neutral and cationic states^a

Structural parameter	8		9	
	Neutral	Cationic	Neutral	Cationic
N–C ₁	1.422	1.392	1.422	1.405
N–C ₃	1.421	1.430	1.421	1.424
N–C ₅	1.421	1.430	1.421	1.424
C ₇ –C ₈	1.412	1.416	1.412	1.419
C ₈ –C _{8'}	1.498	1.469	1.500	1.492
C ₁ –N–C ₃	119.97	121.07	119.96	120.52
C ₁ –N–C ₅	120.00	120.84	119.96	120.52
C ₃ –N–C ₅	120.03	118.08	120.07	118.96
C ₁ –N–C ₃ –C ₄	41.29	48.41	41.23	43.91
C ₁ –N–C ₅ –C ₆	41.72	47.20	41.23	43.91
C ₃ –N–C ₁ –C ₂	41.53	26.94	42.23	33.06
C ₇ –C ₈ –C _{8'} –C _{7'}	88.05	48.11	89.58	79.85

^aFor the bond designation as shown in Fig. 1. The bond lengths are in Å and bond angles in (degree).

Table 2e. Calculated geometrical parameters of compounds **10–12** for the neutral and cationic states^a

Structural parameter	10		11		12	
	Neutral	Cationic	Neutral	Cationic	Neutral	Cationic
N–C ₁	1.417	1.384	1.418	1.404	1.445	1.454
N–C ₃	1.432	1.440	1.401	1.408	1.436	1.427
N–C ₅	1.423	1.430	1.401	1.408	1.436	1.427
C ₇ –C ₈	1.407	1.420	1.405	1.412	1.406	1.406
C ₈ –C _{8'}	1.480	1.454	1.483	1.469	1.485	1.485
C ₉ –C ₁₀					1.339	1.348
C ₁ –N–C ₃	119.58	120.71	125.83	125.77	113.96	113.97
C ₁ –N–C ₅	121.11	121.93	125.83	125.77	113.96	113.97
C ₃ –N–C ₅	118.25	117.24	108.34	108.46	132.08	132.08
C ₁ –N–C ₃ –C ₄	66.51	66.12	1.87	3.84	0.34	0.49
C ₁ –N–C ₅ –C ₆	34.82	45.83	1.87	3.84	0.34	0.49
C ₃ –N–C ₁ –C ₂	26.06	19.07	53.86	44.97	90.59	89.23
C ₇ –C ₈ –C _{8'} –C _{7'}	35.09	21.41	36.69	28.70	38.79	38.80

^aFor the bond designation as shown in Fig. 1. The bond lengths are in Å and bond angles in (degree).

but C₃–N–C₁–C₂ torsional angle decreases comparison with one in the neutral state. In the central biphenyl moiety, the bond length C₈–C_{8'} and torsional angle C₇–C₈–C_{8'}–C_{7'} of the structural geometries in the radical-cation state are smaller and more planar than that of the neutral state. Therefore, the geometry change of compound **1** from the neutral state to the cationic state is very similar to that of BD/TPD type but not to TPA type.

In particular, the compounds in this work (Fig. 2) can be classified as BD/TPD and ISB types. The compound with BD/TPD type is more planar and the phenyl ring closed to the central biphenyl moiety in the radical-cation state, but bond lengths N–C₃ and N–C₅ and the torsional angles C₁–N–C₃–C₄ and C₁–N–C₅–C₆ increase compared to those of the neutral state. According

to Table 2a–2e, compounds **1–11** are BD/TPD type. For the ISB type, the bond lengths N–C₃ and N–C₅ are smaller and the torsional angles C₁–N–C₃–C₄ and C₁–N–C₅–C₆ are bigger in comparison with those at the neutral state. The geometry of the central biphenyl moiety in the neutral state is similar to one in the cationic state and compound **12** is of ISB type.

The addition of a methyl group in the terminal phenyl ring with *meta*- and *para*-substitution has a slight influence on the molecular structure, thus, the geometries of compounds **2** and **3** are similar, but the *ortho*-substitution in the terminal phenyl ring (compound **4**) generated larger steric effect than that of *meta*- and *para*-substitutions (compounds **2** and **3**). In each case, the calculated torsional angle C₁–N–C₃–C₄ of compound

4 is larger than those of compounds **2** and **3**, but the calculated torsional angle and bond length between two phenyl rings during the central biphenyl moiety are similar. The calculated geometries of compounds **4** and **10** (NPB) are also closed.

For compounds **5** and **6**, the addition of methyl groups in the biphenyl moiety 2- and 2,6-substitution results in the rotation of the diphenylamino moiety (NPh₂) on the corresponding N—C₁ bond. For compound **7**, a methyl group is added with *ortho*-substitution in the terminal phenyl ring. Apparently, it is the most effective way to increase the steric effect between the diphenylamino (NPh₂) and central biphenyl moiety, that results in the N—C₁ bond length and the torsional angle C₃—N—C₁—C₂ being larger than those of compound **1** but the geometries of the central biphenyl moiety of compounds **5–7** are similar to compound **1**. For compounds **8** and **9**, the addition of methyl groups on the central phenyl rings with 3,3'- and 3,3',5,5'-substitutions causes the biphenyl groups in these compounds to be more solid. The steric effect of compound **9** is larger than that of compound **8**. The calculated torsional angles C₇—C₈—C₈'—C₇' of compounds **8** and **9** are 88.05 and 89.58° in the neutral state, and there are 48.11 and 79.85° in the cationic state.

Compound **11** (CBP), is widely used as hole-transporting materials.^{35,36} The carbazolyl fragment is planar, but the calculated C₃—N—C₁—C₂ torsional angle between the central biphenyl and the carbazolyl moiety of CBP is larger than that of compound **1** in the neutral and cationic states. For compound **12** (ISB), the iminostilbenyl moiety is also planar but the torsional angle C₃—N—C₁—C₂ between the central biphenyl and the carbazolyl moiety of ISB is larger than that of CBP in the neutral and cationic states (90.59 and 89.23° vs. 53.86 and 44.97°). The

geometry of the central biphenyl moiety of ISB in the neutral state is similar to that of the cationic state.

Ionization potential (*I_p*)

The calculated total energies of the molecules in their optimized geometries of neutral state, assigned to a reference value 0.0 eV and the relative energies (*E*(M) and *E*(M⁺)) are shown in Table 3. The ionization potential (*I_p*) is the energy difference between the cationic and the neutral states based on the optimized geometry for the neutral states. According to Table 3, the calculated *I_p* is almost 1 eV lower than that of the experimental data. However, our calculated *I_p*s of compounds TPA, BD, TPD, and NPB are consistent with other theoretical results.^{18,20} The calculated *I_p*s of compounds **1**, **3**, **5**, and **11** by DFT/BPW91/6-31G(d,p) method, are about 0.25 eV lower than our results, but the trends of the two calculated results are very close.²⁵

The calculated *I_p* of the compound **12**, which is ISB type, is lower than that of the others, except for that of compound **2**. For the TPD type compounds, the order of calculated *I_p* is as following: 11 > 6 > 8 > 5 > 9 > 7 > 4 > 1 > 10 > 3 > 2. This result indicates that the calculated *I_p*s of the compounds with a methyl substituent in the terminal phenyl ring is lower than that of compound **1**, except for that of compound **4**. According to the geometric analysis, the *ortho*-substitution in the terminal phenyl ring generated a more steric effect than those of the *para*- and *meta*-substitution. Conversely, the calculated *I_p*s of the compounds with methyl substituent in the central biphenyl moiety are larger than that of compound **1**.

Table 3. Calculated *E*(M), *E*⁺(M), and ionization potentials *I_p* (energy difference between cation and neutral based on the optimized geometry of neutral state) by the DFT/B3LYP method with the 6-31G* basis set and experimental data of the compounds

Compound	TPA	BD	1	2	3	4	5	6	7	8	9	10	11	12
<i>E</i> ⁺ (M) ^a	6.41	6.07	5.76	5.67	5.73	5.79	5.90	5.97	5.80	5.93	5.88	5.73	6.34	5.69
<i>I_p</i> ^b		6.88 ^d			6.69 ⁱ									
		6.88 ^d												
		6.70 ^g			8.14 ^j									
<i>I_p</i> ^c					5.58 ^e									
	6.35 ^e	5.88 ^e			5.73 ^f									
			5.51 ^h				5.58 ^h					5.60 ^e	6.04 ^h	
	6.42 ^f	6.42 ^f			7.99 ^k									
					5.44 ^h									

^a The total energies of the molecules with their optimized geometries in neutral state are assigned to a reference value *E*(M) = 0.0 eV.

^b Experimental data.

^c Other theoretical calculation.

^d Reference [46].

^e Reference [20].

^f Reference [8].

^g Reference [47].

^h Reference [25].

ⁱ Reference [48].

^j Reference [49].

^k Reference [50].

Reorganization energy

The hole transport in the organic material can be viewed as an electron hopping process, and the dominant transport mechanism is associated with charge hopping between two neighboring molecules, which can be represented by the following:



where, M^+ denotes the molecule in the cationic state, and M^* is the neighboring molecule in the neutral state. This process can be accounted for by the Marcus electron transfer theory and the hole-transfer rate (k_{et}).^{37–42} This may be written as:

$$k_{et} = \left(\frac{4\pi^2}{h} \right) \Delta H_{ab}^2 (4\pi\lambda_+ T)^{-1/2} \exp \left\{ \frac{-\lambda_+}{4kT} \right\} \quad (7)$$

where, λ_+ is the reorganization energy for hole transport, ΔH_{ab} is the electronic coupling matrix element between the donor and acceptor molecules, h and k are Planck's and Boltzmann's constant, respectively. In particular, the ΔH_{ab} and λ_+ play an important role for determining k_{et} . However, it is most likely that ΔH_{ab} would vary over a limited range for analogous molecules.^{43–45} For the TPA-based compounds, ΔH_{ab} are 0.66, 0.55, 0.30, and 0.34 eV for 1,4-bis(diphenylamino)benzene, 1,4-bis[di(4-methoxyphenyl)amino]benzene, 4,4'-bis(diphenylamino)biphenyl, and 4,4'-bis[di(4-methoxyphenyl)amino]biphenyl, respectively.⁴³ In this work, we investigated the influence of molecular conformation in the reorganization energy for these organic diamines only. Since the electronic coupling could be estimated regarding the relative position of the molecules, it still needs the experimental crystal data. We will investigate this property in our further study.

The calculated reorganization energies λ_+ with their components λ_1 and λ_2 , are collected in Table 4. In the pro-

cess λ_1 , the structure changes from a neutral to a cationic state based on the structure in the cationic state. In the process λ_2 , the geometry changes from an optimized cation to an optimized neutral while the compound is in the neutral state. The reorganization energies λ_1 and λ_2 are the differences in energy between the same electronic configurations at different geometries. As expected, in this work, the calculated λ_1 and λ_2 are similar for each compound. For the reorganization energies (λ_+), obviously, the calculated results of compounds TPA, BD, TPD, and NPB also agree well with those calculated by Brédas and Lin.^{18,20} Our calculated λ_+ of compounds **1**, **3**, **5**, and CBP is considerably larger than the BPW1-DFT estimated value. (For example the calculated λ_+ 's of compounds **1**, **3**, **5**, and CBP are 0.27, 0.28, 0.26, and 0.14 eV in this work vs. 0.14, 0.15, 0.14, and 0.07 eV in BPW1-DFT method, respectively.) As expected, this result reflects the sensitivity of the absolute value of the calculated parameters to the employed computational method. Although the computational work neglects solvation factors, there are possible ways to analyze the reorganization energy response based upon structural variation.

Within our calculated data series of compounds, the lowest calculated λ_+ is associated with the rigid molecular framework of compound **12** with the ISB type. Although compound **12** has a biphenyl moiety, its reorganization energy is lower than the others since the terminal phenyl ring may play an important role in determining the Marcus-type reorganization. For the TPD type, compounds **9** and CBP with the rigid molecular framework have the lowest calculated value of λ_+ . According to the geometry analysis, the C₈—C_{8'} bond length of the central biphenyl moiety of compounds ISB, CBP, and **9** in the neutral state are close or vary slightly in comparison to what was found for the cationic state.

Theoretically, the calculated λ_+ of compound **1** is 0.11 eV lower than that of BD. It seems that the terminal

Table 4. $E(M)$, $E^+(M)$, $E(M^+)$, $E^+(M^+)$ and reorganization energies λ_+ , together with its components λ_1 and λ_2 (eV), calculated by the DFT/B3LYP/6-31G⁺ method

Compound	TPA	BD	1	2	3	4	5	6	7	8	9	10	11	12
$E^+(M)^a$	6.41	6.07	5.76	5.67	5.73	5.79	5.90	5.97	5.80	5.93	5.88	5.73	6.34	5.69
$E(M^+)^a$	0.06	0.19	0.14	0.14	0.14	0.17	0.14	0.11	0.11	0.17	0.09	0.17	0.08	0.05
$E^+(M^+)^a$	6.35	5.88	5.63	5.55	5.58	5.65	5.78	5.88	5.72	5.72	5.82	5.62	6.28	5.64
λ_+	0.12	0.38	0.27	0.26	0.28	0.31	0.26	0.19	0.20	0.38	0.15	0.29	0.14	0.09
λ_1	0.06	0.19	0.13	0.12	0.14	0.14	0.12	0.08	0.09	0.21	0.06	0.12	0.06	0.05
λ_2	0.06	0.19	0.14	0.14	0.14	0.17	0.14	0.11	0.11	0.17	0.09	0.17	0.08	0.05
λ_+^b					0.28 ^c									
	0.12 ^c													
		0.38 ^c	0.14 ^e		0.29 ^d		0.14 ^e					0.29 ^c	0.07 ^e	
	0.12 ^d													
					0.13 ^e									

^aTotal energies of the molecular in their optimized geometries in neutral state assigned to a reference value $E(M) = 0.00$ eV.

^bTheoretical calculation.

^cReference [20].

^dReference [18].

^eReference [25].

phenyl ring decreases the λ_+ . The calculated λ_+ values of compounds **1–3** are very close (0.26, 0.27, and 0.28 eV), but these values are higher than that of compound **4**. Thus we conclude the *ortho*-methyl substitution in the terminal phenyl ring (compound **4**) generated a more steric effect than that of the *para*- and *meta*-methyl substitution (compounds **2** and **3**). The 3,3' and 3,3',5,5' methyl substitution on the central biphenyl moiety (compounds **5–7**) has a significant influence on the reorganization energy. Thus, in comparison with the calculated λ_+ of compound **1**, the calculated λ_+ decreases relative to compounds **5–7** in the following order: $1 > 5 > 7 > 6$, and there are also lower calculated λ_1 and higher calculated I_p than those of compounds **5–7**. The methyl substitution on the central biphenyl moiety can be attributed to the lower energy conformation of the compound in the cationic state since it avoids steric interaction between the terminal phenyl ring and methyl groups. The calculated λ_+ of compound **8**, which the 2,2' methyl substitution on the central biphenyl moiety, is close to that of compound **BD** and higher than that of compound **1**. But compound **9** with a 2,2',5,5' methyl substitution on the central biphenyl moiety has a lower calculated λ_+ than those of compounds **BD** and **8** since the 2,2',5,5' methyl substitution on the central biphenyl moiety restricts the attainment of a planar conformation in the biphenyl portion of the molecule, resulting in the differences between the C_8-C_8' and $C_7-C_8-C_8'-C_7'$ of the geometry in the neutral and the cationic states.

If one looks for a predictive tool to determine which geometric parameters dominate reorganization energy, a statistical approach can be adopted, either Simple Linear Regression (SLR, one variable), or MLR (two or more variables). In this work, the geometric parameter difference between the neutral and the cationic states (i.e., a_1 = the $N-C_1$ bond length in the neutral state – the $N-C_1$ bond length in the cationic state) are used as

shown in Table 5. The variables can be divided into 'A' series (the bond length of geometric parameter) and 'B' series (the angle of geometric parameter). The following SLR equation was obtained as following:

$$\begin{aligned}\lambda_+ &= 9.9838 \times a_5 + 0.0376 \\ R^2 &= 0.8644\end{aligned}\quad (8)$$

The result indicates that the reorganization energies have a strong dependence on the difference between the C_8-C_8' bond length of the molecule in the neutral and the cationic states, respectively. Using the MLR, the following equations were obtained:

For A series:

$$\begin{aligned}\lambda_+ &= 5.860948997 \times a_4 \\ &+ 11.449629812 \times a_5 + 0.063709766 \\ R^2 &= 0.9229, R^2_{\text{adj}} = 0.8458\end{aligned}\quad (9)$$

For B series:

$$\begin{aligned}\lambda_+ &= -0.007088289 \times b_4 - 0.012003758 \times b_5 \\ &+ 0.004632957 \times b_7 + 0.086426634 \\ R^2 &= 0.9264, R^2_{\text{adj}} = 0.8527\end{aligned}\quad (10)$$

Both for A and B series:

$$\begin{aligned}\lambda_+ &= 5.329128594 \times a_5 \\ &- 0.030292584 \times b_1 - 0.025040432 \times b_2 \\ &+ 0.003110083 \times b_7 + 0.047702893 \\ R^2 &= 0.9961\end{aligned}\quad (11)$$

In this equations, a_5 is the differences between the C_8-C_8' bond length in the neutral state and the cationic state, b_1 is the differences between the bond angle C_1-N-C_3 , b_2 is the differences between the bond angle C_1-N-C_5 , and b_7 is the differences between the

Table 5. Geometric parameters difference between the neutral and the cationic states of the compounds with TPD type^a

Geometric parameters ^b		Compound with TPD type										
No	Bond length/angle	1	2	3	4	5	6	7	8	9	10	11
a_1	$N-C_1$	0.031	0.031	0.032	0.034	0.025	0.014	0.022	0.030	0.017	0.033	0.014
a_2	$N-C_3$	-0.010	-0.007	-0.009	-0.009	-0.004	0.000	0.000	-0.009	-0.003	-0.008	-0.007
a_3	$N-C_5$	-0.010	-0.010	-0.009	-0.009	-0.001	0.000	0.000	-0.009	-0.003	-0.007	-0.007
a_4	C_7-C_8	-0.013	-0.013	-0.013	-0.013	-0.009	-0.006	-0.009	-0.004	-0.007	-0.013	-0.007
a_5	C_8-C_8'	0.025	0.025	0.025	0.027	0.021	0.014	0.018	0.029	0.008	0.026	0.014
a_1	C_1-N-C_3	-0.82	-1.00	-0.96	-2.71	-1.36	-0.68	-0.26	-1.10	-0.56	-1.13	0.06
a_2	C_1-N-C_5	-0.82	-0.91	-1.00	0.61	-0.84	-0.70	-0.26	-0.84	-0.56	-0.82	0.06
a_3	C_3-N-C_5	1.63	1.89	1.96	1.24	1.70	1.38	0.50	1.95	1.11	1.01	-0.12
a_4	$C_1-N-C_3-C_4$	-5.95	-4.08	-7.08	-0.60	-8.17	-3.56	-1.16	-7.12	-2.68	0.39	-1.97
b_5	$C_1-N-C_5-C_6$	-5.95	-8.48	-6.76	-11.58	-2.90	-3.67	-1.16	-5.48	-2.68	-11.01	-1.97
b_6	$C_3-N-C_1-C_2$	1.93	12.88	14.71	7.53	14.85	10.91	5.22	14.59	9.17	6.99	8.89
b_7	$C_7-C_8-C_8'-C_7'$	14.41	11.49	13.69	16.65	12.34	8.56	11.64	39.94	9.73	13.68	7.99

^aThe difference (a or b) is calculated as following: a (or b) = the geometric parameter in the neutral state – the geometric parameter in the cationic state.

^bThe bond lengths are in Å and bond angles in ° (degree).

torsional angle $C_7-C_8-C_8'-C_7'$ in the neutral state and the cationic state. According to the above calculations, the calculated R^2 and R_{adj}^2 are higher than 0.92 and 0.84, respectively. The R^2 of Eqn 11 is neglected because the independent variable (p) is larger than the data point (n). This results indicate that the reorganization energies have a strong dependence not only on variable a_5 (the differences between the C_8-C_8' bond length in the neutral state and the cationic state) and variable b_7 (the differences between the torsional angle $C_7-C_8-C_8'-C_7'$ in the neutral state and the cationic state) but on b_1 (the differences between the bond angle C_1-N-C_3) and b_2 (the differences between the bond angle C_1-N-C_5) variables. Besides, Eqn 11 demonstrates that the reorganization energies (λ_+) increase as variable a_5 and b_7 , but the reorganization energies (λ_+) decrease as b_1 and b_2 . Therefore, according to the above calculation results, our calculation results do not support the Brédas¹⁸ and Lin²⁰ calculation of TPD which indicate that the conformation of the central biphenyl moiety is dominating molecular property in determining the relative gas-phase reorganization energy. In principle, the conformation of the terminal phenyl moiety is also one dominative variable in determining this relative reorganization energy. The above calculation results indicated that there exists a good linear relationship between four geometrical parameters and reorganization energies of the organic diamines in this work.

CONCLUSION

The DFT B3LYP/6-31G* calculation on a series of tetra(aryl)benzidine derivatives was used to reveal the impact of molecular conformation on reorganization energies and the charge transfer process in these tetra(aryl)benzidine-based hole-transport materials. We conclude that there are ISB and BD/TPD types of the geometric difference of the organic diamines during the relaxation processes: ISB type has a lower reorganization energy than that of the BD/TPD type. The reorganization energy of a BD/TPD type material may be tuned with not only the conformation of the central biphenyl moiety, but also with one of the terminal phenyl rings. According to the statistical analysis, four geometric parameters, playing a significant role in determining the reorganization energy, are the differences between the geometric parameters C_8-C_8' , $C_7-C_8-C_8'-C_7'$, C_1-N-C_3 , and C_1-N-C_5 in the neutral and the cationic states. By the differential control of the reorganization energies, one can design compounds with desired transport properties. According to the Marcus theory, ideal hole-transporting compounds with small λ_+ can be realized for the future development of OLEDs. Furthermore, this calculation may be the molecular design for developing a new optoelectric material.

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